

PATENT COOPERATION TREATY

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

United States Patent and Trademark
Office
(Box PCT)
Crystal Plaza 2
Washington, DC 20231
ÉTATS-UNIS D'AMÉRIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 08 June 1999 (08.06.99)	
International application No. PCT/IL98/00491	Applicant's or agent's file reference PDS
International filing date (day/month/year) 08 October 1998 (08.10.98)	Priority date (day/month/year) 12 October 1997 (12.10.97)
Applicant ALMOG, Yaacov et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:
25 April 1999 (25.04.99)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was

☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

<p>The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland</p> <p>Facsimile No.: (41-22) 740.14.35</p>	<p>Authorized officer P. Regis</p> <p>Telephone No.: (41-22) 338.83.38</p>
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PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference PDS	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/IL98/00491	International filing date (day/month/year) 08/10/1998	Priority date (day/month/year) 12/10/1997
International Patent Classification (IPC) or national classification and IPC G03G7/00		
Applicant INDIGO N.V. et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.


2. This REPORT consists of a total of 5 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 8 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand 25/04/1999	Date of completion of this report 24. 01. 00
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Consee, O Telephone No. +49 89 2399 2675



INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/IL98/00491

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1,2,6-9 as originally filed

3-5 as received on 12/11/1999 with letter of 10/11/1999

Claims, No.:

1-41 as received on 12/11/1999 with letter of 10/11/1999

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-12,14-41
	No:	Claims	13
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-41
Industrial applicability (IA)	Yes:	Claims	1-41
	No:	Claims	

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

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2. Citations and explanations

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/IL98/00491

ad V: Novelty and inventive step

1. As the applicant correctly states in the letter of 10.11.99, the newly filed claims are merely rearranged (and, in claims 13 and 33, the reference to "styrene butadiene copolymer" has been removed).
2. The present as well as the original claims relate to three groups:
 - a substrate comprising a sheet of plastic having an underlayer of a defined material, and an overlayer of an undefined material (claims 1 and 30);
 - a substrate comprising a sheet of plastic (claim 13: BOPP) having an underlayer of undefined material, and an overcoating layer of a defined material (claims 13, 4 and 6);
 - a substrate comprising a BOPP sheet and an outer coating of a defined material (claim 33).
3. From the document EP-A-0 458 481 (D1), claims, a substrate suitable for printing a toner image thereon is known which comprises a sheet of plastic (page 2, lines 23 to 58: polypropylene (BOPP), polyethylene, polyvinylchloride, PET, polycarbonate) which is preferably biaxially oriented (line 48), an underlayer coating (lacquer layer) comprising a polymer material which has crosslinkable functional groups, e.g. amine and trihydroxy silyl groups (page 3, lines 2-9), and an overlayer coating comprising a polymer material to which a toner image can be fused and fixed (page 4, line 42 - page 5, line 38: acrylic acid copolymers, vinyl pyridine copolymer, styrene butadiene copolymer).
4. Having regard to this state of the art, the subject matter of present claims 1 and 30 lacks inventive step (Article 33(3) PCT) since the "polymers containing trihydroxy silyl groups (page 3, line 8) differ from the "polymer chosen from the group consisting of ... a silane coupling agent" only in that they are already hydrolyzed (see, page 1, penultimate paragraph of applicant's letter). No invention can be seen in this difference.

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/IL98/00491

5. The subject matter of claim 13 lacks novelty (Article 33(2) PCT) with regard to D1 - see, above point 3. The subject matter of claims 4 and 6 differ from this state of the art in essence in that the overlayer does not contain wax, pigment or particulate matter. No invention (Article 33(3) PCT) can be seen in this difference since the skilled person would add or not such additives if required.
6. The subject matter of claim 33 lacks inventive step with regard to D1 since the skilled person would apply the outer coating on a BOPP sheet directly or on an intermediate layer on grounds of his normal experimental activity.
7. The printing method of claims 37 to 41 is conventional, comprises only usual process steps in the technical field of toner printing and does not involve an inventive step, in particular since the substrate per se is not inventive.
8. The additional features of the dependent claims are partly known from D1 and, moreover, conventional in the present technical field. They do not add inventive matter to the subject matter of the independent claims.

weight percent of 20%. In preferred embodiments of the invention, the overlayers are free of silica, talc or other such fillers and free of wax or pigments.

A second aspect of some preferred embodiments of the invention relates to substrates which are coated with ethylene acrylic acid copolymer, polyvinyl pyridine or styrene butadiene copolymer, and especially to substrates coated with ethylene acrylic acid copolymer with reduced acidity. Such coated substrates may, in some preferred embodiments of the invention, be plastic substrates such as PET or BOPP or, in other embodiments of the invention, may be paper. Preferably, the overlayer consists substantially only of these materials and more preferably consists substantially only of one of these materials.

A third aspect of some preferred embodiments of the invention relates to the printing of images, preferably toner images and more preferably liquid toner images, on substrates of the invention or which are produced in accordance with the invention. This printing is preferably by transfer of the toner images to the substrate from an intermediate transfer member, to which it was transferred from an imaging surface. Preferred toners are based on one or more of ethylene vinyl acetate (EVA) copolymers, copolymers of ethylene and α , β - ethyleneically unsaturated acid selected from the group consisting of acrylic and methacrylic acids and ionomers such as are produced under the trade name of Surlyn, by Dupont.

There is therefore provided in accordance with a preferred embodiment of the invention, a substrate suitable for printing a toner image thereon, comprising:

a sheet of plastic;

an underlayer coating, on the sheet of plastic, comprising a first polymer material comprising a polymer chosen from the group consisting of amine terminated polyamide, a silane coupling agent and amino propyl triethoxy silane;

an overlayer coating, directly on the underlayer, comprising a second polymer material and having an outer surface to which a toner image can be fused and fixed.

There is further provided, in accordance with a preferred embodiment of the invention a substrate suitable for printing a toner image thereon, comprising:

a sheet of plastic;

an underlayer coating, on the sheet of plastic, comprising a first polymer material;

an overlayer coating, directly on the underlayer, comprising a second polymer material and having an outer surface to which a toner image can be fused and fixed, the second polymer consisting essentially of a polymer chosen from the group consisting of ethylene acrylic acid copolymer, polyvinyl pyridine and styrene butadiene copolymer.

Preferably, the first polymer material comprises a polymer chosen from the group consisting of amine terminated polyamide, a silane coupling agent and amino propyl triethoxy silane.

Preferably, the sheet of plastic is PET. Alternatively, the sheet of plastic is BOPP.

5 Alternatively, the sheet of plastic is polyethylene. Alternatively, the sheet of plastic is vinyl. Alternatively, the sheet of plastic is polycarbonate.

In a preferred embodiment of the invention, the overlayer comprises ethylene acrylic acid copolymer. Preferably, the ethylene acrylic acid copolymer has an acrylic acid comonomer percentage weight of less than 18%. Alternatively, the ethylene acrylic acid
10 copolymer has an acrylic acid comonomer percentage weight of less than 16%.

Alternatively or additionally, the ethylene acrylic acid copolymer has an acrylic acid comonomer percentage weight of more than 8%. Alternatively, the ethylene acrylic acid copolymer has an acrylic acid comonomer percentage weight of more than 12%.

In a preferred embodiment of the invention, the overlayer comprises polyvinyl
15 pyridine. Alternatively, the overlayer comprises styrene butadiene copolymer.

In a preferred embodiment of the invention, the underlayer comprises amine terminated polyamide. Alternatively, the underlayer comprises a silane coupling agent. Alternatively, the underlayer comprises amino propyl triethoxy silane.

In a preferred embodiment of the invention, the underlayer has a weight of between 0.1
20 and 1 grams per square meter. Alternatively or additionally, the underlayer has a weight of between about 0.3 and 0.5 grams per square meter.

In a preferred embodiment of the invention, the overlayer has a weight of between 0.1 and 10 grams per square meter. Alternatively or additionally, the overlayer has a weight of between 0.2 and 2 grams per square meter. Preferably, the overlayer has a weight of between
25 about 0.25 and about 0.35 grams per square meter.

Preferably, the overlayer is substantially wax and pigment free.

Preferably, the overlayer is substantially free of particulate matter. Preferably, the underlayer is substantially free of particulate matter. More preferably, both the overlayer and the underlayer are free of particulate matter.

30 Preferably, the substrate comprises only two coating layers.

There is further provided in accordance with a preferred embodiment of the invention, a method of producing a coated substrate which a toner image can be adhered comprising:

coating a sheet of plastic with a first polymer material as an underlayer, the underlayer comprising a polymer chosen from the group consisting of amine terminated polyamide, a silane coupling agent and amino propyl triethoxy silane;

directly overcoating the underlayer with an second polymer material to form an overlayer coating on the underlayer, the overlayer having an outer surface to which a toner image can be adhered and fixed.

There is further provided, in accordance with a preferred embodiment of the invention, a method of producing a coated substrate which a toner image can be adhered comprising:

coating a sheet of plastic with a first polymer material as an underlayer;

directly overcoating the underlayer with an second polymer material to form an overlayer coating on the underlayer, the overlayer having an outer surface to which a toner image can be adhered and fixed, the second polymer consisting essentially of a polymer chosen from the group consisting of ethylene acrylic acid copolymer, polyvinyl pyridine and styrene butadiene copolymer.

Preferably, the first polymer material comprises a polymer chosen from the group consisting of amine terminated polyamide, a silane coupling agent and amino propyl triethoxy silane.

There is also provided in accordance with a preferred embodiment of the invention, a substrate comprising a sheet chosen from the group consisting of PET, BOPP, polycarbonate, polyethylene and vinyl and an outer coating consisting substantially only of a polymer chosen from the group consisting of ethylene acrylic acid copolymer, polyvinyl pyridine and styrene butadiene copolymer.

Preferably, the sheet is a PET sheet. Alternatively, the sheet is a BOPP sheet. Alternatively, the sheet is a polycarbonate sheet. Alternatively, the sheet is a polyethylene sheet. Alternatively, the sheet is a vinyl sheet.

Preferably, the coating comprises polyvinyl pyridine. Alternatively, the coating comprises styrene butadiene copolymer. Alternatively, the coating comprises ethylene acrylic acid copolymer. Preferably, the ethylene acrylic acid copolymer has an acrylic acid comonomer percentage weight of less than 18%.

There is also provided in accordance with a preferred embodiment of the invention, a substrate comprising a sheet and a coating of ethylene acrylic acid copolymer having an acrylic acid comonomer percentage weight of less than 18%.

CLAIMS

1. A substrate suitable for printing a toner image thereon, comprising:

a sheet of plastic;

an underlayer coating, on the sheet of plastic, comprising a first polymer material comprising a polymer chosen from the group consisting of amine terminated polyamide, a silane coupling agent and amino propyl triethoxy silane;

an overlayer coating, directly on the underlayer, comprising a second polymer material and having an outer surface to which a toner image can be fused and fixed.

2. A substrate according to claim 1 wherein the overlayer is substantially free of particulate matter.

3. A substrate according to claim 1 or claim 2 wherein the overlayer is substantially wax and pigment free.

4. A substrate suitable for printing a toner image thereon, comprising:

a sheet of plastic;

an underlayer coating, on the sheet of plastic, comprising a first polymer material;

an overlayer coating, directly on the underlayer, comprising a second polymer material and having an outer surface to which a toner image can be fused and fixed, the second polymer consisting essentially of a polymer chosen from the group consisting of ethylene acrylic acid copolymer, polyvinyl pyridine and styrene butadiene copolymer, characterized in that the overlayer is substantially wax and pigment free.

5. A substrate according to claim 4 wherein the overlayer is substantially free of particulate mater.

6. A substrate suitable for printing a toner image thereon, comprising:

a sheet of plastic;

an underlayer coating, on the sheet of plastic, comprising a first polymer material;

an overlayer coating, directly on the underlayer, comprising a second polymer material and having an outer surface to which a toner image can be fused and fixed, the second polymer consisting essentially of a polymer chosen from the group consisting of ethylene acrylic acid copolymer, polyvinyl pyridine and styrene butadiene copolymer,
 5 characterized in that the overlayer is substantially free of particulate matter.

7. A substrate according to any of the preceding claims wherein the sheet of plastic is polyethylene.

10 8. A substrate according to any of claims 1-6 wherein the sheet of plastic is vinyl.

9. A substrate according to any of claims 1-6 wherein the sheet of plastic is polycarbonate.

15 10. A substrate according to any of claims 1-6 wherein the sheet of plastic is PET.

11. A substrate according to any of claims 1-6, wherein the sheet of plastic is BOPP.

12. A substrate according to any of the preceding claims wherein the overlayer comprises
 20 styrene butadiene copolymer.

13. A substrate suitable for printing a toner image thereon, comprising:

a sheet of BOPP plastic;

an underlayer coating, on the sheet of plastic, comprising a first polymer material;

25 an overlayer coating, directly on the underlayer, comprising a second polymer material and having an outer surface to which a toner image can be fused and fixed, the second polymer consisting essentially of a polymer chosen from the group consisting of ethylene acrylic acid copolymer and polyvinyl pyridine.

30 14. A substrate according to any of claims 1-11 or 13, wherein the overlayer comprises ethylene acrylic acid copolymer.

15. A substrate according to claim 14 wherein the ethylene acrylic acid copolymer has an acrylic acid comonomer percentage weight of less than 18%.
- 5 16. A substrate according to claim 14 wherein the ethylene acrylic acid copolymer has an acrylic acid comonomer percentage weight of less than 16%.
17. A substrate according to any of claims 14-15 wherein the ethylene acrylic acid copolymer has an acrylic acid comonomer percentage weight of more than 8%.
- 10 18. A substrate according to any of claims 14-15 wherein the ethylene acrylic acid copolymer has an acrylic acid comonomer percentage weight of more than 12%.
19. A substrate according to any of claims 1-11 or 13 wherein the overlayer comprises polyvinyl pyridine.
- 15 20. A substrate according to any of the preceding claims wherein the underlayer comprises amine terminated polyamide.
21. A substrate according to any of claims 1-19 wherein the underlayer comprises a silane coupling agent.
- 20 22. A substrate according to any of claims 1-19 wherein the underlayer comprises amino propyl triethoxy silane.
23. A substrate according to any of the preceding claims wherein the underlayer has a weight of between 0.1 and 1 grams per square meter.
- 25 24. A substrate according to any of the preceding claims wherein the underlayer has a weight of between about 0.3 and 0.5 grams per square meter.
- 30 25. A substrate according to any of the preceding claims wherein the overlayer has a weight of between 0.1 and 10 grams per square meter.

26. A substrate according to any of the preceding claims wherein the overlayer has a weight of between 0.2 and 2 grams per square meter.

27. A substrate according to claim 26 wherein the overlayer has a weight of between about 0.25 and about 0.35 grams per square meter.

28. A substrate according to any of the preceding claims wherein the underlayer is substantially free of particulate matter.

29. A substrate according to any of the preceding claims comprising only two coating layers.

30. A method of producing a coated substrate which a toner image can be adhered comprising:

coating a sheet of plastic with a first polymer material as an underlayer, the underlayer comprising a polymer chosen from the group consisting of amine terminated polyamide, a silane coupling agent and amino propyl triethoxy silane;

directly overcoating the underlayer with an second polymer material to form an overlayer coating on the underlayer, the overlayer having an outer surface to which a toner image can be adhered and fixed.

31. A method according to claim 30 wherein the coated substrate is a substrate according to any of claims 1-29.

32. A substrate produced according to the method of claim 30 or claim 31.

33. A substrate comprising a sheet of BOPP and an outer coating consisting substantially only of a polymer chosen from the group consisting of ethylene acrylic acid copolymer, and polyvinyl pyridine.

34. A substrate according to claim 33 wherein the coating comprises polyvinyl pyridine.

35. A substrate according to claim 33 wherein the coating comprises ethylene acrylic acid copolymer.

36. A substrate according to claim 35 wherein the ethylene acrylic acid copolymer has an acrylic acid comonomer percentage weight of less than 18%.

37. A printing method comprising:

providing a substrate according to any of claims 1-29 or 32-36 or produced according to claim 30 or claim 31; and

printing a toner image on the substrate.

38. A printing method according to claim 37 wherein the toner image is a liquid toner image.

39. A printing method according to claim 37 or claim 38 wherein printing comprises transferring the toner image to the substrate using heat and pressure.

40. A printing method according to claim 37 or 38 wherein printing comprises electrostatically transferring the toner image to the substrate.

41. A printing method according to any of claims 37-40 and comprising:

forming the image on an image forming surface;

transferring the image from the image forming surface to an intermediate transfer member; and

transferring the image from the intermediate transfer member to the substrate.

PATENT COOPERATION TREATY

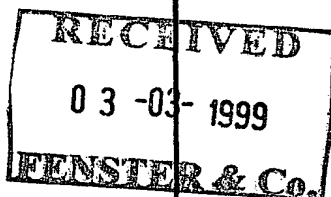
From the INTERNATIONAL SEARCHING AUTHORITY

PCT

To:
FENSTER & COMPANY PATENT
ATTORNEYS, LTD
P.O.Box 10256
Petach Tikva 49002
ISRAEL

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL SEARCH REPORT
OR THE DECLARATION

(PCT Rule 44.1)



Date of mailing
(day/month/year) 22/02/1999

Applicant's or agent's file reference
PDS

FOR FURTHER ACTION See paragraphs 1 and 4 below

International application No.
PCT/IL 98/00491

International filing date
(day/month/year) 08/10/1998

Applicant
INDIGO N.V. et al.

1. ☒ The applicant is hereby notified that the International Search Report has been established and is transmitted with.

Filing of amendments and statement under Article 19:

The applicant is entitled, if he so wishes, to amend the claims of the International Application (see Rule 46):

When? The time limit for filing such amendments is normally 2 months from the date of transmittal of the International Search Report; however, for more details, see the notes on the accompanying sheet.

Where? Directly to the International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland
Facsimile No.: (41-22) 740.14.35

For more detailed instructions, see the notes on the accompanying sheet.

2. ☐ The applicant is hereby notified that no International Search Report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.

3. ☐ **With regard to the protest** against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

☐ the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.

☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. **Further action(s):** The applicant is reminded of the following:

Shortly after **18 months** from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90 bis.1 and 90 bis.3, respectively, before the completion of the technical preparations for international publication.

Within **19 months** from the priority date, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later).

Within **20 months** from the priority date, the applicant must perform the prescribed acts for entry into the national phase before all designated Offices which have not been elected in the demand or in a later election within 19 months from the priority date or could not be elected because they are not bound by Chapter II.

Name and mailing address of the International Searching Authority



European Patent Office, P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
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Authorized officer

Nathalie Ostwinkel

NOTES TO FORM PCT/ISA/220

These Notes are intended to give the basic instructions concerning the filing of amendments under article 19. The Notes are based on the requirements of the Patent Cooperation Treaty, the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the PCT Applicant's Guide, a publication of WIPO.

In these Notes, "Article", "Rule", and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions respectively.

INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the latter to be published for the purposes of provisional protection or has another reason for amending the claims before international publication. Furthermore, it should be emphasized that provisional protection is available in some States only.

What parts of the international application may be amended?

Under Article 19, only the claims may be amended.

During the international phase, the claims may also be amended (or further amended) under Article 34 before the International Preliminary Examining Authority. The description and drawings may only be amended under Article 34 before the International Examining Authority.

Upon entry into the national phase, all parts of the international application may be amended under Article 28 or, where applicable, Article 41.

When?

Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

Where not to file the amendments?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been/is filed, see below.

How?

Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Administrative Instructions, Section 205(b)).

The amendments must be made in the language in which the international application is to be published.

What documents must/may accompany the amendments?

Letter (Section 205(b)):

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confused with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

The letter must be in English or French, at the choice of the applicant. However, if the language of the international application is English, the letter must be in English; if the language of the international application is French, the letter must be in French.

NOTES TO FORM PCT/ISA/220 (continued)

The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped), whether

- (i) the claim is unchanged;
- (ii) the claim is cancelled;
- (iii) the claim is new;
- (iv) the claim replaces one or more claims as filed;
- (v) the claim is the result of the division of a claim as filed.

The following examples illustrate the manner in which amendments must be explained in the accompanying letter:

1. [Where originally there were 48 claims and after amendment of some claims there are 51]:
"Claims 1 to 29, 31, 32, 34, 35, 37 to 48 replaced by amended claims bearing the same numbers; claims 30, 33 and 36 unchanged; new claims 49 to 51 added."
2. [Where originally there were 15 claims and after amendment of all claims there are 11]:
"Claims 1 to 15 replaced by amended claims 1 to 11."
3. [Where originally there were 14 claims and the amendments consist in cancelling some claims and in adding new claims]:
"Claims 1 to 6 and 14 unchanged; claims 7 to 13 cancelled; new claims 15, 16 and 17 added." or
"Claims 7 to 13 cancelled; new claims 15, 16 and 17 added; all other claims unchanged."
4. [Where various kinds of amendments are made]:
"Claims 1-10 unchanged; claims 11 to 13, 18 and 19 cancelled; claims 14, 15 and 16 replaced by amended claim 14; claim 17 subdivided into amended claims 15, 16 and 17; new claims 20 and 21 added."

"Statement under article 19(1)" (Rule 46.4)

The amendments may be accompanied by a statement explaining the amendments and indicating any impact that such amendments might have on the description and the drawings (which cannot be amended under Article 19(1)).

The statement will be published with the international application and the amended claims.

It must be in the language in which the international application is to be published.

It must be brief, not exceeding 500 words if in English or if translated into English.

It should not be confused with and does not replace the letter indicating the differences between the claims as filed and as amended. It must be filed on a separate sheet and must be identified as such by a heading, preferably by using the words "Statement under Article 19(1)."

It may not contain any disparaging comments on the international search report or the relevance of citations contained in that report. Reference to citations, relevant to a given claim, contained in the international search report may be made only in connection with an amendment of that claim.

Consequence if a demand for international preliminary examination has already been filed

If, at the time of filing any amendments under Article 19, a demand for international preliminary examination has already been submitted, the applicant must preferably, at the same time of filing the amendments with the International Bureau, also file a copy of such amendments with the International Preliminary Examining Authority (see Rule 62.2(a), first sentence).

Consequence with regard to translation of the international application for entry into the national phase

The applicant's attention is drawn to the fact that, where upon entry into the national phase, a translation of the claims as amended under Article 19 may have to be furnished to the designated/elected Offices, instead of, or in addition to, the translation of the claims as filed.

For further details on the requirements of each designated/elected Office, see Volume II of the PCT Applicant's Guide.

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference PDS	FOR FURTHER ACTION		see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.
International application No. PCT/IL 98/00491	International filing date (day/month/year) 08/10/1998	(Earliest) Priority Date (day/month/year) 12/10/1997	
Applicant INDIGO N.V. et al.			

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. ☐ Certain claims were found unsearchable (see Box I).

2. ☐ Unity of invention is lacking (see Box II).

3. ☐ The international application contains disclosure of a **nucleotide and/or amino acid sequence listing** and the international search was carried out on the basis of the sequence listing

☐ filed with the international application.

☐ furnished by the applicant separately from the international application,

☐ but not accompanied by a statement to the effect that it did not include matter going beyond the disclosure in the international application as filed.

☐ Transcribed by this Authority

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6. The figure of the **drawings** to be published with the abstract is:

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INTERNATIONAL SEARCH REPORT

International Application No.
PCT/IL 98/00491

A. CLASSIFICATION OF SUBJECT MATTER

G 03 G 7/00, G 03 G 13/16, G 03 G 13/20, G 03 G 13/22

According to International Patent Classification (IPC) or to both national classification and IPC 6

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

G 03 G, B 32 B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0458481 A2 (IMPERIAL CHEMICAL INDUSTRIES PLC) 27 November 1991 (27.11.91), claims, page 2, lines 23-57, page 3, lines 2-9, 33, 34, page 4, line 42 - page 5, line 38, page 5, line 58 - page 6, lines 2, 31, 32.	2, 4, 6- 8, 14, 15, 27, 29, 31- 34, 36- 40, 49, 50, 52
A	--	1, 28
X	EP 0789281 A2 (MOBIL OIL CORPORATION) 13 August 1997 (13.08.97), claims, page 3, lines 2-4, page 4, lines 25-37, page 5, lines 1-15, page 6, lines 35-37.	2, 4, 6, 9-13, 21-23, 27, 29, 31-34, 37, 41- 50, 52, 53

☒ Further documents are listed in the continuation of box C.

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- "&" document member of the same patent family

Date of the actual completion of the international search
30 December 1998

Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

International Application No

PCT/IL 98/00491

-2-

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	US 5126198 A (SCHINKEL et al.) 30 June 1992 (30.06.92), claims, column 3, lines 1-12, column 4, lines 54-56.	2, 9- 13, 27, 29, 31- 33, 41- 46
A	--	1
X	DE 2454047 A1 (COPYER CO., LTD.) 15 May 1975 (15.05.75), claims 1, 7, page 2, lines 11- 15, page 3, lines 1-5, page 6, lines 21-24, page 7, lines 2-6, page 9, lines 1-8.	2, 9- 13, 15, 29, 31- 33, 40- 46, 49, 52
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A	EP 0048481 A2 (TEIJIN LIMITED) 31 March 1982 (31.03.82), claims 1, 13, 15, 33-36, page 1, lines 4-9, page 4, lines 7-26.	1, 4, 17, 18, 28, 30- 34

ANHANG

zum internationalen Recherchen-
bericht über die internationale
Patentanmeldung Nr.

ANNEX

to the International Search
Report to the International Patent
Application No.

ANNEXE

au rapport de recherche inter-
national relatif à la demande de brevet
international n°

PCT/IL 98/00491 SAE 211083

In diesem Anhang sind die Mitglieder
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members relating to the patent documents
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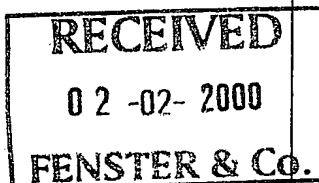
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IMPORTANT NOTIFICATION

International application No.
PCT/IL98/00491

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08/10/1998

Priority date (day/month/year)
12/10/1997

Applicant
INDIGO N.V. et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : G03G 7/00, 13/16, 13/20, 13/22	A1	(11) International Publication Number: WO 99/19773 (43) International Publication Date: 22 April 1999 (22.04.99)
(21) International Application Number: PCT/IL98/00491 (22) International Filing Date: 8 October 1998 (08.10.98) (30) Priority Data: 121951 12 October 1997 (12.10.97) IL PCT/IL97/00391 27 November 1997 (27.11.97) IL (71) Applicant (for all designated States except US): INDIGO N.V. [NL/NL]; Limburglaan Street 5, NL-6221 SH Maastricht (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): ALMOG, Yaacov [IL/IL]; Halutz Street 2, 76251 Rehovot (IL). BRANDISS, Sergio [IL/IL]; Yavetz Street 11, 76252 Rehovot (IL). (74) Agents: FENSTER, Paul et al.; Fenster & Company Patent Attorneys, Ltd., P.O. Box 10256, 49002 Petach Tikva (IL).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: COATING SYSTEM FOR SUBSTRATES (57) Abstract A substrate suitable for printing a toner image thereon, comprising: a sheet of plastic; an underlayer coating, on the sheet of plastic, comprising a first polymer material preferably comprising a polymer chosen from the group consisting of amine terminated polyamide, a silane coupling agent and amino propyl triethoxy silane; an overlayer coating, directly on the underlayer, comprising a second polymer material and having an outer surface to which a toner image can be fused and fixed, the second polymer preferably consisting essentially of a polymer chosen from the group consisting of ethylene acrylic acid copolymer, polyvinyl pyridine and styrene butadiene copolymer.		

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COATING SYSTEM FOR SUBSTRATES

FIELD OF THE INVENTION

The present invention is related to the field of printing and in particular to a method of coating substrates to improve adhesion of toner images thereto.

BACKGROUND OF THE INVENTION

Problems of transfer and adhesion of toner images and in particular of liquid toner images, to substrates, is well known. Transfer of images may be effected by electrostatic transfer of toner particles to the substrate, either from an imaging surface such as a photoreceptor or from an image transfer member. Alternatively, image transfer may be effected by heat and pressure, generally from an intermediate transfer member to which the image is first transferred from the imaging surface. Image transfer from an intermediate transfer member, on which the image is generally in a molten state, is often problematic. Usually, some treatment of the substrate surface is required in order to enable good transfer and fixing.

Transfer and adhesion of toner is improved by chemical compatibility of the toner and the substrate for example, chemical bonding by acid-base interaction or chemical similarity leading to mutual bonding.

A common solution to transfer and adhesion problems is the coating of a substrate with an adhesion enhancer, which has an affinity for both the toner material and the substrate. For example, the adhesion of the above mentioned toner types to PET and BOPP can be greatly enhanced by coating the substrates with a layer of Macromelt 6239 (Henkel) which is an amine terminated polyamide. This material adheres well to the substrate and has a high affinity for the toner particle polymer as well. However, it has been found that the shelf life of such coated substrates is limited and the quality of the transfer of toner from an intermediate transfer member to the substrate degrades with time. This aging process of the coating does not seem to effect the adhesion of images which are already transferred to the substrate.

However, as is well known in the art, such substrate processing does not always lead to satisfactory results, especially in digital electrostatic printing.

EP Patent Publication EP 0 789 281, the disclosure of which is incorporated herein by reference, describes a coating system for polypropylene in which the polypropylene is coated with polyethylene and then with ethylene-acrylic acid and minor amounts of filler such as talc or silica and wax and/or pigment.

EP Patent Publication EP 048 481 describes a coating system for coating a polymeric substrate with a first lacquer layer, preferably containing a particulate material. The lacquer layer is overcoated with a toner receptive layer containing a copolymer comprising styrene and/or a styrene derivative and at least one ethylenically unsaturated co-monomer copolymerisable therewith, the copolymer containing at least one free functional acid group. The toner preferably comprises an additional acrylic and/or metacrylic polymer to improve the ink receptivity of the layer. Optionally, an adhesion promoting layer may be situated between the lacquer layer and the polymeric substrate.

US Patent 5,126,198 describes a coated substrate that is not described as being suitable for forming toner images thereon. Rather this material is used as a heat laminatable multi-layer film. The outer, heat laminatable layer comprises a mixture of polymers.

SUMMARY OF THE INVENTION

One aspect of some preferred embodiments of the present invention is a novel approach to the improvement of transferability and/or adhesion of images to substrates, especially plastic substrates.

In a broad view of some preferred embodiments of the invention, a double coating is employed, with an underlayer having a high affinity for the substrate and an overlayer having a high affinity for the toner material. The two layers have a high affinity for each other.

In an exemplary embodiment of this aspect of the invention, the underlayer is a layer of an amine terminated polyamide such as Macromelt 6239 (Henkel) which was mentioned in the background of the invention. The upper layer is formed of material which has a high affinity for toner particles and which is also adheres well to the underlayer. As indicated above, an amine terminated polyamide has a high affinity for a wide range of materials so that this seldom is a problem. Furthermore, the above mentioned deterioration of the properties of the amine terminated polyamide with time does not exist when it is coated with the overlayer.

Exemplary materials which are useful as overlayers include ethylene acrylic acid copolymer, polyvinyl pyridine and styrene butadiene copolymer. Preferably, the overlayer consists substantially only of these materials and more preferably consists substantially only of one of these materials. It is noted that these materials adhere rather poorly to untreated PET, BOPP, polycarbonate, polyethylene and vinyl. For some applications it is useful to reduce the degree of acidity of the ethylene acrylic acid copolymer, preferably by Saponification to a level of preferably between 8 and 18% acrylic acid comonomer weight percent, more preferably between 10 and 16%. Unmodified material typically has a acrylic acid comonomer

weight percent of 20%. In preferred embodiments of the invention, the overlayers are free of silica, talk or other such fillers and free of wax or pigments.

A second aspect of some preferred embodiments of the invention relates to substrates which are coated with ethylene acrylic acid copolymer, polyvinyl pyridine or styrene butadiene copolymer, and especially to substrates coated with ethylene acrylic acid copolymer with reduced acidity. Such coated substrates may, in some preferred embodiments of the invention, be plastic substrates such as PET or BOPP or, in other embodiments of the invention, may be paper. Preferably, the overlayer consists substantially only of these materials and more preferably consists substantially only of one of these materials.

A third aspect of some preferred embodiments of the invention relates to the printing of images, preferably toner images and more preferably liquid toner images, on substrates of the invention or which are produced in accordance with the invention. This printing is preferably by transfer of the toner images to the substrate from an intermediate transfer member, to which it was transferred from an imaging surface. Preferred toners are based on one or more of ethylene vinyl acetate (EVA) copolymers, copolymers of ethylene and α , β - ethyleneically unsaturated acid selected from the group consisting of acrylic and methacrylic acids and ionomers such as are produced under the trade name of Surlyn, by Dupont.

There is therefore provided in accordance with a preferred embodiment of the invention, a substrate suitable for printing a toner image thereon, comprising:

- a sheet of plastic;
- an underlayer coating, on the sheet of plastic, comprising a first polymer material comprising a polymer chosen from the group consisting of amine terminated polyamide, a silane coupling agent and amino propyl triethoxy silane;
- an overlayer coating, directly on the underlayer, comprising a second polymer material and having an outer surface to which a toner image can be fused and fixed.

There is further provided, in accordance with a preferred embodiment of the invention a substrate suitable for printing a toner image thereon, comprising:

- a sheet of plastic;
- an underlayer coating, on the sheet of plastic, comprising a first polymer material;
- an overlayer coating, directly on the underlayer, comprising a second polymer material and having an outer surface to which a toner image can be fused and fixed, the second polymer consisting essentially of a polymer chosen from the group consisting of ethylene acrylic acid copolymer, polyvinyl pyridine and styrene butadiene copolymer.

Preferably, the first polymer material comprises a polymer chosen from the group consisting of amine terminated polyamide, a silane coupling agent and amino propyl triethoxy silane.

Preferably, the sheet of plastic is PET. Alternatively, the sheet of plastic is BOPP.
5 Alternatively, the sheet of plastic is polyethylene. Alternatively, the sheet of plastic is vinyl. Alternatively, the sheet of plastic is polycarbonate.

In a preferred embodiment of the invention, the overlayer comprises ethylene acrylic acid copolymer. Preferably, the ethylene acrylic acid copolymer has an acrylic acid comonomer percentage weight of less than 18%. Alternatively, the ethylene acrylic acid
10 copolymer has an acrylic acid comonomer percentage weight of less than 16%.

Alternatively or additionally, the ethylene acrylic acid copolymer has an acrylic acid comonomer percentage weight of more than 8%. Alternatively, the ethylene acrylic acid copolymer has an acrylic acid comonomer percentage weight of more than 12%.

In a preferred embodiment of the invention, the overlayer comprises polyvinyl
15 pyridine. Alternatively, the overlayer comprises styrene butadiene copolymer.

In a preferred embodiment of the invention, the underlayer comprises amine terminated polyamide. Alternatively, the underlayer comprises a silane coupling agent. Alternatively, the underlayer comprises amino propyl triethoxy silane.

In a preferred embodiment of the invention, the underlayer has a weight of between 0.1
20 and 1 grams per square meter. Alternatively or additionally, the underlayer has a weight of between about 0.3 and 0.5 grams per square meter.

In a preferred embodiment of the invention, the overlayer has a weight of between 0.1 and 10 grams per square meter. Alternatively or additionally, the overlayer has a weight of between 0.2 and 2 grams per square meter. Preferably, the overlayer has a weight of between
25 about 0.25 and about 0.35 grams per square meter.

Preferably, the overlayer is substantially wax and pigment free.

Preferably, the overlayer is substantially free of particulate matter. Preferably, the underlayer is substantially free of particulate matter. More preferably, both the overlayer and the underlayer are free of particulate matter.

30 Preferably, the substrate comprises only two coating layers.

There is further provided in accordance with a preferred embodiment of the invention, a method of producing a coated substrate which a toner image can be adhered comprising:

coating a sheet of plastic with a first polymer material as an underlayer, the underlayer comprising a polymer chosen from the group consisting of amine terminated polyamide, a silane coupling agent and amino propyl triethoxy silane;

5 directly overcoating the underlayer with an second polymer material to form an overlayer coating on the underlayer, the overlayer having an outer surface to which a toner image can be adhered and fixed.

There is further provided, in accordance with a preferred embodiment of the invention, a method of producing a coated substrate which a toner image can be adhered comprising:

coating a sheet of plastic with a first polymer material as an underlayer;

10 directly overcoating the underlayer with an second polymer material to form an overlayer coating on the underlayer, the overlayer having an outer surface to which a toner image can be adhered and fixed, the second polymer consisting essentially of a polymer chosen from the group consisting of ethylene acrylic acid copolymer, polyvinyl pyridine and styrene butadiene copolymer.

15 Preferably, the first polymer material comprises a polymer chosen from the group consisting of amine terminated polyamide, a silane coupling agent and amino propyl triethoxy silane.

20 There is also provided in accordance with a preferred embodiment of the invention, a substrate comprising a sheet chosen from the group consisting of PET, BOPP, polycarbonate, polyethylene and vinyl and an outer coating consisting substantially only of a polymer chosen from the group consisting of ethylene acrylic acid copolymer, polyvinyl pyridine and styrene butadiene copolymer.

25 Preferably, the sheet is a PET sheet. Alternatively, the sheet is a BOPP sheet. Alternatively, the sheet is a polycarbonate sheet. Alternatively, the sheet is a polyethylene sheet. Alternatively, the sheet is a vinyl sheet.

Preferably, the coating comprises polyvinyl pyridine. Alternatively, the coating comprises styrene butadiene copolymer. Alternatively, the coating comprises ethylene acrylic acid copolymer. Preferably, the ethylene acrylic acid copolymer has an acrylic acid comonomer percentage weight of less than 18%.

30 There is also provided in accordance with a preferred embodiment of the invention, a substrate comprising a sheet and a coating of ethylene acrylic acid copolymer having an acrylic acid comonomer percentage weight of less than 18%.

Preferably, an ethylene acrylic acid copolymer, as described above, has an acrylic acid comonomer percentage weight of less than 16%. Alternatively, the ethylene acrylic acid copolymer has an acrylic acid comonomer percentage weight of more than 8%.

5 Preferably, the ethylene acrylic acid copolymer has an acrylic acid comonomer percentage weight of more than 12%.

Preferably, the coating, as described above, has a weight of between 0.1 and 0.4 grams per square meter. Preferably, the coating has a weight of between about 0.25 and about 0.35 grams per square meter.

10 There is also provided in accordance with a preferred embodiment of the invention, a printing method comprising:

providing a substrate, as described above; and
printing a toner image on the substrate.

Preferably, the toner image is a liquid toner image. Alternatively or additionally, printing comprises transferring the toner image to the substrate using heat and pressure.
15 Alternatively, printing comprises electrostatically transferring the toner image to the substrate.

In a preferred embodiment of the invention, the printing method comprises:
forming the image on an image forming surface;
transferring the image from the image forming surface to an intermediate transfer member; and

20 transferring the image from the intermediate transfer member to the substrate.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

A substrate according to a preferred embodiment of the present invention, on which a toner image is to be printed, comprises a plastic or other sheet coated with an underlayer having a high affinity for the substrate and an overlayer having a high affinity for the toner
25 material. The two layers have a high affinity for each other.

One preferred, but non-limiting, method for producing such a substrate uses an underlayer of amine terminated polyamide and an overlayer of ethylene acrylic acid copolymer.

The underlayer

To 950 grams of 1-Propanal add 50 grams of Macromelt 6239 (Henkel), amine terminated polyamide, while stirring the mixture. Heat the material to between 40°C and 50°C until a homogeneous and clear 5% solids solution is obtained.

5 This material is applied to a substrate (for example an optionally corona treated BOPP substrate) by coating the substrate with the 5% solids solution and allowing the solution to dry, leaving a coating of preferably between about 0.1 and 0.3 grams of solid per square meter. This coating should be uniform. The coating may be applied by any one of the available methods of coating and, for example, using a rotogravure coating system. Alternatively a
10 flexographic printing system can be used to apply the coating with the settings of the printer controlling the thickness of the coating. However any other suitable coating process (double blade direct applicator, etc.) can be used. Other solution concentrations and other variations on the above described method can also be used.

While thinner and thicker coatings could be used, thinner coatings are not always
15 effective and thicker coatings are more difficult to apply and expensive.

After application of the solution the coating is dried, preferably by an integral heater in the coating apparatus.

The overlayer

To 465 gm of deionized water add 200 g of isopropyl alcohol. This reaction is
20 exothermic. After the mixture cools, add it to 335 g of a dispersion of MP 4990 (32-35%) as supplied by Michelman.

The dispersion is coated onto the underlayer by any convenient coating process, as for the underlayer, to give a coating of between approximately 0.3 - 0.5 grams per square meter although thinner coatings can be used.. If a double coating apparatus is available, the overlayer
25 may be applied immediately over a dried underlayer.

After application of the overlayer solution the coating is dried, preferably by using the dryer integral in the coater. Other drying methods can also be used.

While the above formulation of overlayer material is suitable for printing on web fed material, it will adhere to surfaces with which it comes into contact, while hot, after printings,
30 as, for example, an exit roller. To reduce the hot adhesivity, the degree of acidity of the ethylene acrylic acid copolymer, is reduced, preferably by Saponification to a level of preferably between 8 and 18% acrylic acid comonomer weight percent, more preferably between 10 and 16%. Unmodified material typically has a acrylic acid comonomer weight

percent of 20%. This modified material can be used to directly coat paper and plastic substrates which do not require the adhesion promotion properties of the underlayer.

Other underlayer materials, for example, a silane coupling agent such as amino propyl triethoxy silane, may be used. The primary requirement for an underlayer is that it have high
5 adhesion to the substrate and to the overlayer.

Other suitable overlayer materials include Polyvinyl pyridine (Molecular weight 40,000 to 200,000) (Scientific Polymer Products). Additionally Styronal PK 8717 (BASF) (styrene butadiene copolymer) can be used as the overlayer. These material are preferably coated at a weight of approximately 0.5 grams per square meter.

10 Various bonding mechanisms can be utilized in various embodiments of the present invention. In the above example, the underlayer and overlayer are base and acid respectively. The toner described below is also acidic; however, the toner forms a strong chemical bond with the overlayer. Other materials, in accordance with preferred embodiment of the invention, utilize other types of bonding.

15 In general, a coating thickness (after drying) of between 0.1 to 10 micrometers is preferred. More preferably, the thickness is between 0.2 to 2 microns.

The coated substrates of the present invention are useful with a wide range of toner material which do not transfer easily to and/or adhere well to PET and BOPP. Preferred toners are based on one or more of ethylene vinyl acetate (EVA) copolymers, copolymers of ethylene
20 and α , β - ethyleneically unsaturated acid selected from the group consisting of acrylic and methacrylic acids and ionomers such as are produced under the trade name of Surlyn, by Dupont.

One preferred method of forming a toner is the following:

1) Solubilization

25 1400 grams of Nucrel 925 (ethylene copolymer by Dupont) and 1400 grams of Isopar L (Exxon) are thoroughly mixed in an oil heated Ross double planetary mixer at at least 24 RPM for 1.5 hours, with the oil temperature at 130°C. 1200 grams of preheated Isopar L is added and mixing is continued for an additional hour. The mixture is cooled to 45°C, while stirring is continued, over a period of several hours, to form a viscous material.

2) Milling and Grinding

762 grams of the result of the solubilizing step are ground in a 1S attritor (Union Process Inc. Acron, Ohio), charged with 3/16" carbon steel balls, at 250 RPM, together with 66.7 grams of Mogul L carbon black (Cabot), 6.7 grams of BT583D (blue pigment produced by Cookson), 5 grams of aluminum tri stearate and an additional 1459.6 grams of Isopar L, for eight hours at 30°C.

3) Continuation of Grinding

34.5 grams of ACumist A-12 is added and grinding is continued for an additional 4-12 hours. The resulting particles are fibrous particles having a measured diameter in the range of 1-3 micrometers.

The resulting material is diluted with additional Isopar L and Marcol 82 to give a working developer in which the dry solids portion is about 1.7% and in which the overall ratio of Isopar L to Marcol is between about 50:1 and 500:1, normally about 100:1.

Charge director as described in US patent application 07/915,291 (utilizing Lecithin BBP and ICIG3300B) and in WO 94/02887, in an amount equal to 40 mg/gm of solids, is added to charge the tone particles. Other charge directors and additional additives, as known in the art may also be used.

In a preferred embodiment of the invention the substrate is printed using an intermediate transfer member to transfer images to the substrate and to fuse and fix them thereto. Preferred apparatus for such printing are the E-Print 1000 and the E-Print Omnius printers marketed by Indigo NV.

The present invention has been described utilizing preferred embodiments thereof. It should be understood that the details of the coating processes and exact formulations of the coatings and liquid toners are meant to be exemplary in nature and not to limit the claims. In particular the invention also includes materials which are listed in the summary and claims for the substrate, the underlayer, the overlayer and the toner, as well as different combinations of materials chosen from the four groups of materials. When used in the claims, the words "comprise," "include" and "have" and their conjugations mean "including, but not necessarily limited to."

CLAIMS

1. A substrate suitable for printing a toner image thereon, comprising:
a sheet of plastic;
5 an underlayer coating, on the sheet of plastic, comprising a first polymer material comprising a polymer chosen from the group consisting of amine terminated polyamide, a silane coupling agent and amino propyl triethoxy silane;
an overlayer coating, directly on the underlayer, comprising a second polymer material and having an outer surface to which a toner image can be fused and fixed.
10
2. A substrate suitable for printing a toner image thereon, comprising:
a sheet of plastic;
an underlayer coating, on the sheet of plastic, comprising a first polymer material;
an overlayer coating, directly on the underlayer, comprising a second polymer material
15 and having an outer surface to which a toner image can be fused and fixed, the second polymer consisting essentially of a polymer chosen from the group consisting of ethylene acrylic acid copolymer, polyvinyl pyridine and styrene butadiene copolymer.
3. A substrate according to claim 2 wherein the first polymer material comprises a
20 polymer chosen from the group consisting of amine terminated polyamide, a silane coupling agent and amino propyl triethoxy silane.
4. A substrate according to any of the preceding claims wherein the sheet of plastic is PET.
25
5. A substrate according to any of claims 1-3 wherein the sheet of plastic is BOPP.
6. A substrate according to any of claims 1-3 wherein the sheet of plastic is polyethylene.
- 30 7. A substrate according to any of claims 1-3 wherein the sheet of plastic is vinyl.
8. A substrate according to any of claims 1-3 wherein the sheet of plastic is polycarbonate.

9. A substrate according to any of the preceding claims wherein the overlayer comprises ethylene acrylic acid copolymer.
- 5 10. A substrate according to claim 9 wherein the ethylene acrylic acid copolymer has an acrylic acid comonomer percentage weight of less than 18%.
11. A substrate according to claim 9 wherein the ethylene acrylic acid copolymer has an acrylic acid comonomer percentage weight of less than 16%.
- 10 12. A substrate according to any of claims 9-11 wherein the ethylene acrylic acid copolymer has an acrylic acid comonomer percentage weight of more than 8%.
13. A substrate according to any of claims 9-11 wherein the ethylene acrylic acid
15 copolymer has an acrylic acid comonomer percentage weight of more than 12%.
14. A substrate according to any of claims 1-8 wherein the overlayer comprises polyvinyl pyridine.
- 20 15. A substrate according to any of claims 1-8 wherein the overlayer comprises styrene butadiene copolymer.
16. A substrate according to any of the preceding claims wherein the underlayer comprises amine terminated polyamide.
- 25 17. A substrate according to any of claims 1-15 wherein the underlayer comprises a silane coupling agent.
18. A substrate according to any of claims 1-15 wherein the underlayer comprises amino
30 propyl triethoxy silane.
19. A substrate according to any of the preceding claims wherein the underlayer has a weight of between 0.1 and 1 grams per square meter.

20. A substrate according to any of the preceding claims wherein the underlayer has a weight of between about 0.3 and 0.5 grams per square meter.

5 21. A substrate according to any of the preceding claims wherein the overlayer has a weight of between 0.1 and 10 grams per square meter.

22. A substrate according to any of the preceding claims wherein the overlayer has a weight of between 0.2 and 2 grams per square meter.

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23. A substrate according to claim 22 wherein the overlayer has a weight of between about 0.25 and about 0.35 grams per square meter.

15 24. A substrate according to any of the preceding claims wherein the overlayer is substantially wax and pigment free.

25. A substrate according to any of the preceding claims wherein the overlayer is substantially free of particulate matter.

20 26. A substrate according to any of the preceding claims wherein the underlayer is substantially free of particulate matter.

27. A substrate according to any of the preceding claims comprising only two coating layers.

25

28. A method of producing a coated substrate which a toner image can be adhered comprising:

30 coating a sheet of plastic with a first polymer material as an underlayer, the underlayer comprising a polymer chosen from the group consisting of amine terminated polyamide, a silane coupling agent and amino propyl triethoxy silane;

directly overcoating the underlayer with an second polymer material to form an overlayer coating on the underlayer, the overlayer having an outer surface to which a toner image can be adhered and fixed.

29. A method of producing a coated substrate which a toner image can be adhered comprising:

coating a sheet of plastic with a first polymer material as an underlayer;

5 directly overcoating the underlayer with an second polymer material to form an overlayer coating on the underlayer, the overlayer having an outer surface to which a toner image can be adhered and fixed, the second polymer consisting essentially of a polymer chosen from the group consisting of ethylene acrylic acid copolymer, polyvinyl pyridine and styrene butadine copolymer.

10 30. A method according to claim 29 wherein the first polymer material comprises a polymer chosen from the group consisting of amine terminated polyamide, a silane coupling agent and amino propyl triethoxy silane.

15 31. A method according to any of claims 28-30 wherein the coated substrate is a substrate according to any of claims 1-27.

32. A substrate produced according to the method of any of claims 28-31.

20 33. A substrate comprising a sheet chosen from the group consisting of PET, BOPP, polycarbonate, polyethylene and vinyl and an outer coating consisting substantially only of a polymer chosen from the group consisting of ethylene acrylic acid copolymer, polyvinyl pyridine and styrene butadine copolymer.

25 34. A substrate according to claim 33 wherein the sheet is a PET sheet.

35. A substrate according to claim 33 wherein the sheet is a BOPP sheet.

36. A substrate according to claim 33 wherein the sheet is a polycarbonate sheet.

30 37. A substrate according to claim 33 wherein the sheet is a polyethylene sheet.

38. A substrate according to claim 33, wherein the sheet is a vinyl sheet.

39. A substrate according to any of claims 33-38 wherein the coating comprises polyvinyl pyridine.

5 40. A substrate according to any of claims 33-38 wherein the coating comprises styrene butadiene copolymer.

41. A substrate according to any of claims 33-38 wherein the coating comprises ethylene acrylic acid copolymer.

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42. A substrate according to claim 41 wherein the ethylene acrylic acid copolymer has an acrylic acid comonomer percentage weight of less than 18%.

15 43. A substrate comprising a sheet and a coating consisting substantially only of ethylene acrylic acid copolymer having an acrylic acid comonomer percentage weight of less than 18%.

44. A substrate according to any of claims 41-43 wherein the ethylene acrylic acid copolymer has an acrylic acid comonomer percentage weight of less than 16%.

20 45. A substrate according to any of claims 41-44 wherein the ethylene acrylic acid copolymer has an acrylic acid comonomer percentage weight of more than 8%.

46. A substrate according to any of claims 41-45 wherein the ethylene acrylic acid copolymer has an acrylic acid comonomer percentage weight of more than 12%.

25

47. A substrate according to any of claims 33-46 wherein the coating has a weight of between 0.1 and 0.4 grams per square meter.

30 48. A substrate according to claim 47 wherein the coating has a weight of between about 0.25 and about 0.35 grams per square meter.

49. A printing method comprising:

providing a substrate according to any of claims 1-27 or 32-48 or produced according to any of claims 28-31; and
printing a toner image on the substrate.

5 50. A printing method according to claim 49 wherein the toner image is a liquid toner image.

51. A printing method according to claim 49 or claim 50 wherein printing comprises transferring the toner image to the substrate using heat and pressure.

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52. A printing method according to claim 49 or 50 wherein printing comprises electrostatically transferring the toner image to the substrate.

53. A printing method according to any of claims 49-52 and comprising:

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forming the image on an image forming surface;
transferring the image from the image forming surface to an intermediate transfer member; and
transferring the image from the intermediate transfer member to the substrate.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/IL 98/00491

A. CLASSIFICATION OF SUBJECT MATTER

G 03 G 7/00, G 03 G 13/16, G 03 G 13/20, G 03 G 13/22

According to International Patent Classification (IPC) or to both national classification and IPC ⁶

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

G 03 G, B 32 B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☒ Further documents are listed in the continuation of box C.

☐ Patent family members are listed in annex.

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- * "E" earlier document but published on or after the international filing date
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- * "O" document referring to an oral disclosure, use, exhibition or other means
- * "P" document published prior to the international filing date but later than the priority date claimed

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- * "&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/IL 98/00491

-2-

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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ANHANG

ANNEX

ANNEXE

zum internationalen Recherchen-
bericht über die internationale
Patentanmeldung Nr.

to the International Search
Report to the International Patent
Application No.

au rapport de recherche inter-
national relatif à la demande de brevet
international n°

PCT/IL 98/00491 SAE 211083

In diesem Anhang sind die Mitglieder
der Patentfamilien der im obenge-
nannten internationalen Recherchenbericht
angeführten Patentedokumente angegeben.
Diese Angaben dienen nur zur Unter-
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This Annex lists the patent family
members relating to the patent documents
cited in the above-mentioned inter-
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La présente annexe indique les
membres de la famille de brevets
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national visée ci-dessus. Les renseigne-
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